COMPOSITION AND METHOD FOR
METAL COLORING PROCESS

Background of the Invention

Field of the Invention

This invention relates to the formation of a hybrid chemical conversion coating on ferrous metal substrates, consisting of an iron/oxygen rich intermediate coating and a top layer of magnetite. This invention also relates to ferrous metal substrates coated according to the presently disclosed process. This invention further includes the oxidation solution used in oxidizing the iron/oxygen rich intermediate coating to the final magnetite containing top layer. This invention also includes a seven-step procedure for preparing a ferrous metal substrate with a magnetite containing coating.

Description of the Related Art

The established art of coloring ferrous metals has revolved principally around methods for producing black coatings. Since the 1950's, the most commonly used commercial method for blackening ferrous metals has been the caustic black oxidizing process. This method will be examined, along with the ferrous oxalate conversion coating on ferrous metal substrate and the iron phosphatizing process.

Caustic black oxidizing: This process uses sodium hydroxide, sodium nitrate and sodium nitrite as oxidizing agents, operating at about pH 14, at temperatures of about 285 - 305° F. A black coating is formed during exposures of about 10 - 30 minutes. This process forms a magnetite (Fe_3O_4) deposit, approximately 1 micron thick, by reacting with the metallic iron substrate in situ. Although the process produces high quality black finishes when operated properly, it has the disadvantage of requiring high temperatures and highly concentrated solutions (700-1000 grams per liter) to carry out the reaction.

During the course of operation, this reaction consumes oxidizing salts and the solution boils off significant quantities of water. These materials must be added back to the solution to maintain proper operating conditions. However, adding sodium hydroxide to water, being a highly exothermic reaction, is quite hazardous because the operating solution is already boiling. Likewise, adding make-up water to a solution which is already at 285 - 305° F causes the water to instantly boil if not added very slowly and carefully. Consequently, the operation of the process poses severe safety hazards for personnel, due to the dangers involved in normal system operation and maintenance. These hazardous conditions may be difficult to justify in the manufacturing environments of modern industry. In addition, normal operating conditions typically entail heavy sludge formation in the process tank, difficulty in disposal of the spent solutions (due to extremely high concentrations), and variable quality on certain metals, including tool steel alloys, sintered iron articles or other porous substrates. Unless highly skilled operators are employed, this process may result in poor quality finishes. It is common to see undesirable red/brown finishes on certain alloys or salt leaching on porous substrates. As a

1 result, the process is largely relegated to use by professional metal finishers who possess
2 specialized knowledge and experience in dealing with hazardous materials.

3   <u>Ferrous oxalate conversion coating:</u> This coating was originally developed for use as a
4 metal forming lubricant and anti-galling coating for mating parts. The finish is generally applied
5 at about ambient temperatures, is about 1 micron thick and opaque gray in color. When sealed
6 with a rust preventative topcoat, the oxalate offers some degree of corrosion protection. Used
7 more commonly in the 1950's, the oxalate process is rarely used today, having given way to the
8 several phosphate processes on the market, which offer more beneficial properties in terms of
9 lubrication and/or paint adhesion.

10   <u>Iron phosphate conversion coating:</u> These coatings are widely used in the metal finishing
11 industry as pretreatments to enhance paint adhesion and corrosion resistance on ferrous metal
12 substrates. With a coating thickness of about 1 micron, the amorphous deposit is formed at
13 temperatures of about 70 - 130° F by a mildly acid solution which may also contain cleaning
14 agents. The iron phosphate process has proven to be a very versatile and effective option in paint
15 lines and other metal finishing process lines.

16   There have been several patents issued over the years which relate to blackening
17 processes. For purposes of this invention, however, reference is made to prior patents which are
18 directly related to oxalate and phosphate conversion coatings on ferrous metal substrates and to
19 the caustic black oxidizing of ferrous metal substrates:

	U.S. Patent No.	Date	Subject
20			
21	2,774,696	12/18/56	Oxalate Coatings on Chromium Alloy Substrates
22	2,791,525	5/7/57	Chlorate Accelerated Oxalate Coatings on Ferrous
23			Metals for Forming Lubricity and Paint Adhesion
24	2,805,696	9/10/57	Molybdenum Accelerated Oxalate Coatings
25	2,835,616	5/20/58	Method of Processing Ferrous Metals to Form
26			Oxalate Coatings
27	2,850,417	9/2/58	m-Nitrobenzene Sulfonate Accelerated Oxalates on
28			Ferrous Metals
29	2,960,420	11/15/60	Composition and Process For Black Oxidizing of
30			Ferrous Metals Using Mercapto-Based Accelerators
31			and naphthalene based Wetting Agents
32	3,121,033	2/11/64	Oxalates on Stainless Steels
33	3,481,762	12/2/69	Manganous Oxalates Sealed with Graphite and Oil
34			for Forming Lubricity
35	3,632,452	9/17/58	Stannous Accelerated Oxalates on Stainless Steels
36	3,649,371	3/14/72	Fluoride Modified Oxalates
37	3,806,375	4/23/75	Hexamine/SO_2 Accelerated Oxalates
38	3,879,237	4/22/75	Manganese, Fluoride, Sulfide Accelerated Oxalates
39	3,899,367	8/12/75	Composition and Process For Black Oxidizing Of
40			Ferrous Metals Using Molybdic Acids On Tool
41			Steels

1	4,017,335	4/12/77	pH Stabilized Composition and Method For Iron
2			Phosphatizing Of Ferrous Metal Surfaces
3	5,104,463	4/14/92	Composition and Process For Caustic Oxidizing Of
4			Stainless Steels Using Chromate Accelerators

6   All but one of these oxalate patents pertain to the formation of a ferrous oxalate
7 conversion coating on ferrous metal substrates using various accelerators. These oxalates are
8 intended for use as functional coatings to aid in assembly or provide forming lubricity, etc.
9 These coatings serve as deformable or crushable boundary layers at the metal surface, thereby
10 protecting the base metal during contact with another surface.

11   The caustic black oxidizing patents focus on compositions and processes which oxidize
12 the metallic iron substrate to a magnetite, Fe_3O_4, as described in U.S. Patent No. 2,960,420.
13 Actually, when examining the stoichiometry of the Fe_3O_4, one can see that the iron is not in
14 either a purely ferrous (II) or ferric (III) oxidation state. Perhaps a more precise description of
15 the material is that of a mixed salt, ferrosoferric oxide, or $FeO \cdot Fe_2O_3$, which exhibits both ferrous
16 and ferric iron. The conventional caustic oxidizing processes all depend on the ability of the
17 operating solution to oxidize metallic iron to both ferrous (II) and ferric (III) oxidation states to
18 form the mixed oxide $FeO \cdot Fe_2O_3$.

19   The process described in U.S. Patent No. 4,017,335 is representative of the state of the
20 art, focusing on the primary phosphatizing mechanism which is well known to those skilled in
21 the art. In addition, this same patent illustrates incorporation of a cleaning agent and pH
22 stabilizer into the oxidizing solution to effectively clean lightly soiled ferrous articles and iron
23 phosphatize them in a single step.

24 <div align="center">SUMMARY OF THE INVENTION</div>

25   This invention provides an alternative method and composition for forming aesthetically
26 pleasing and protective, as well as functionally useful, magnetite coatings on ferrous metal
27 substrates. The mechanism involves a first oxidation to provide an intermediate coating on the
28 metallic iron substrate, such as a ferrous oxalate (or other dicarboxylate) or an iron phosphate
29 coating, whose primary purpose is to act as a precursor to the magnetite. By providing a surface
30 abundant in both molecular iron and molecular oxygen, the intermediate coating facilitates the
31 formation of the magnetite (in a second oxidation), thereby requiring a blackening solution with
32 much less oxidizing potential than is necessary with conventional oxidizing solutions in terms of
33 concentration, operating temperatures and contact times. It is important to note that the
34 oxidizing solution used in the second oxidation of this invention is not able to blacken the metal
35 substrate without the intermediate coating (from the first oxidation) in place. The overall
36 oxidizing potential of the second oxidizing solution in this invention is so much lower than that
37 of conventional solutions that no reaction will take place unless the intermediate coating (from
38 the first oxidation) has been applied first. After the second oxidation, the coating may be
39 topcoated with a lubricant, rust preventative compound or polymer-based topcoat appropriate to
40 the end use of the article.

1   A process according to this invention for forming a hybrid conversion coating on a
2 ferrous metal substrate, encompasses applying to the substrate an intermediate coating rich in
3 molecular iron and oxygen, and then contacting the intermediate coated substrate with an
4 aqueous solution of oxidizing agents to form a magnetite containing surface. The substrate is
5 coated with a water insoluble molecular oxygen and iron enriched intermediate coating by a first
6 oxidation which comprises contacting the substrate with an aqueous solution of a dicarboxylic
7 acid, or of a reagent selected from phosphoric acid, pyrophosphoric acid and salts thereof, or
8 mixtures thereof, at an appropriate concentration, pH, temperature and time to achieve a desired
9 water insoluble molecular oxygen and iron enriched intermediate coating. The intermediate
10 coated substrate is then subjected to a second oxidation by contacting with an aqueous solution
11 of an oxidizing agent at a concentration, pH, temperature and time to form the desired amount of
12 magnetite. The coated substrate may then be sealed with a topcoat.

13   A coated colored ferrous metal article according to this invention has a surface formed by
14 two treatments, wherein the first treatment is an iron/oxygen-enriched intermediate oxidized
15 coating applied to a ferrous substrate, and the second treatment is a further oxidation of the first
16 coating to magnetite.
17
18   An oxidation solution for oxidizing at least a portion of an iron/oxygen enriched
19 intermediate coating on a ferrous substrate to magnetite according to this invention comprises an
20 aqueous solution of oxidizing agents selected from alkali metal compounds of hydroxide, nitrate,
21 and nitrite and mixtures thereof, and optionally further including an additional component
22 selected from an accelerator, a metal chelator, a surface tension reducer and mixtures thereof.

23   This invention also provides a seven-step procedure for forming a hybrid conversion
24   coating on a ferrous metal substrate, comprising the steps of:

25   (1)   subjecting the ferrous metal substrate to treatment selected from cleaning,
26 degreasing, descaling, and mixtures thereof;

27   (2)   rinsing the substrate from step (1) with water;

28   (3)   subjecting the substrate from step (2) to a first oxidation to form a molecular
29 iron/oxygen enriched intermediate coating;

30   (4)   rinsing the substrate from step (3) with water;

31   (5)   subjecting the substrate from step (4) to a second oxidation to form a surface
32   which is predominantly magnetite, Fe_3O_4;

33   (6)   rinsing the substrate from step (5) with water; and

34   (7)   sealing the substrate with an appropriate topcoat.
35

DETAILED DESCRIPTION OF THE INVENTION

A ferrous metal substrate is defined herein as any metallic substrate whose composition is primarily iron. This may include steel, stainless steel, cast iron, gray and ductile iron, and sintered iron of all alloys.

The iron/oxygen rich intermediate coating applied to the substrate in the first oxidation can be formed using any of the water soluble dicarboxylic acids, especially aliphatic dicarboxylic acids generally of up to about five carbon atoms, such as oxalic, malonic, succinic, tartaric acids, and others and mixtures thereof. There are advantages and disadvantages to each dicarboxylic acid. For example, oxalic acid is generally available at the lowest cost and is the most reactive. However, oxalic acid tends to form intermediate coatings of relatively coarse grain, with large crystals and the intermediate coating usually benefits from the addition of a grain refiner to the first oxidation, such as alkali metal compounds of tartrate, tripolyphosphate, molybdate, citrate, polyphosphate and thiocyanate, including sodium potassium tartrate, sodium citrate, sodium molybdate, sodium polyphosphate and sodium thiocyanate. An intermediate coating with a denser crystal structure is considered preferable because it tends to produce a resultant black finish (after the second oxidation) that is cleaner, with less ruboff, and also thinner, which is desirable for most machine/tool applications. A mixture of two or more dicarboxylic acids tends to favor the formation of a denser microcrystalline structure on the metal surface, perhaps obviating the need for a grain refiner. However, the costs of many of the commercial grades of other dicarboxylic acids are significantly higher than that of oxalic acid, the solubilities are lower and the reaction rates significantly lower as well. In fact, these other longer chain aliphatic dicarboxylic acids may actually require the use of accelerators instead of or in addition to grain refiners in order to be workable in a practical sense. Suitable accelerators for use in the first oxidation include organic and inorganic nitro compounds, and alkali-metal compounds of citrate, molybdate, polyphosphate, thiocyanate, chlorate, and sulfide, such as sodium chlorate, sodium molybdate, and organic nitro compounds.

Alternatively, the iron/oxygen rich intermediate coating can consist of other coatings such as iron phosphate. The iron phosphate coating does not appear to be quite as effective as the dicarboxylate coatings, because the iron phosphate deposit tends to be amorphous rather than crystalline. Though the adhesion of iron phosphate to the substrate is generally satisfactory, the amorphous iron phosphate deposit tends to be less durable and less resistant to rubbing and/or wear factors, thus appearing to have more sooty ruboff in the final prepared article. The advantages of the phosphate coating, however, include the lower commercial cost of the chemicals and the ability to operate at higher (less acidic) pH levels. These advantages improve worker safety aspects of the process line. Appropriate reagents for deposition of the water insoluble phosphate-based coating include phosphoric acid, as well as alkali metal acid phosphates, alkali metal pyrophosphates, primary alkanol amine phosphates and mixtures thereof. Typically, the iron phosphate solutions are able to operate at about pH 3.0 - 5.0 (dicarboxylates operate at about pH 1.0 - 2.0), at temperatures of about 70 - 130° F, and contact times of 1 - 3 minutes.

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1   An intermediate coating with a more densely formed crystal structure tends to concentrate
2 or increase the availability of iron and oxygen and thus tends to favor the formation of the
3 magnetite in the second oxidation. A more densely formed crystal structure tends to facilitate the
4 blackening of certain ferrous alloys of lower reactivity, such as heat-treated steels or more highly
5 alloyed steels. Typically, these types of steels tend to be less reactive because the concentration
6 of metallic iron at the surface is lower than that encountered with cast irons or softer steels.
7 Consequently, it is considered preferable to design the composition of the iron/oxygen rich
8 intermediate coating solution to maximize the crystal structure density of the intermediate
9 coating, thereby overcoming any low initial reactivity of iron substrate.

10   The operating temperature of the intermediate coating solution also has an effect on the
11 reaction rate -- higher temperatures tend to increase the reaction rate. Experimental evidence
12 indicates that, although many iron alloys can be successfully processed at ambient temperatures,
13 certain less reactive alloys benefit from application of the intermediate coating at temperatures of
14 about 100 - 150° F to overcome any low initial reactivity of the metal surface.

15   At suitable grain refiner for the first oxidation has been found to be an alkali metal
16 tartrate, typically at a concentration of about 0.1 - 1.0 gram per liter. the accelerator is selected
17 from organic and inorganic nitro compounds, alkali metal salts of citrate, molybdate,
18 polyphosphate, thiocyanate, chlorate and sulfide at concentrations of about 0.5 - 5.0 grams per
19 liter. A suitable accelerator for the first oxidation may be selected from organic and inorganic
20 nitro compounds, typically at concentrations of about 0.1 - 5.0 grams per liter.

21   In summary, then, the composition of the intermediate coating solution (the first
22 oxidation) may take many forms, depending on the cost, solubility and activity level of the
23 chemicals used, the pH of the solution and coarseness of the crystal structure, as well as the
24 initial reactivity of the iron metal alloy, the value or intended use of the article and other factors
25 deemed pertinent to each application.

26   After coating the article with the iron/oxygen rich intermediate coating, the article is
27 blackened by contacting it with a second oxidation solution at elevated temperatures to form the
28 magnetite. Experimental evidence indicates that most of the intermediate coating remains intact
29 on the article surface after the second oxidation, with only a small portion of the coating reacting
30 to form magnetite. Although the exact reaction mechanism of the second oxidation is not clearly
31 understood, it is believed that portions of the intermediate coating react with the second
32 oxidation solution to form magnetite interspersed within the crystal structure of the coating.
33 Some magnetite may be chemically bonded to molecules of the intermediate coating.

34   The first oxidation is believed to convert metallic iron, to Fe(II), when the coating is a
35 ferrous dicarboxylate, or to a mixture of Fe(II) and Fe(III) when the coating is an iron phosphate.
36 Accordingly, in this specification the dicarboxylate coating is designated as "ferrous," because
37 the iron is in the ferrous or Fe(II) oxidation state, while the phosphate coating is designated more
38 broadly as "iron," because the iron is in both the ferrous, Fe(II), and ferric, Fe(III), oxidation
39 states. It is reasonable to believe that the primary iron oxide formed is Fe_3O_4, although it is
40 possible that other iron oxides are formed, such as FeO and Fe_2O_3, and other compounds, such as

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FeS, SnS and SnO (due to the possible presence of sulfur and tin in the reagent solutions), all of which can be gray/black in color. The oxides of iron tend to be non-stoichiometric, and readily interconvertible with each other. The tendency of each of the iron oxides to be nonstoichiometric is due to some extent to the intimate relationship between their structures. The structure of each oxide may be visualized as a cubic close-packed array of oxide ions with a certain number of Fe(II) and/or Fe(III) ions distributed among octahedral and tetrahedral holes. Each of the iron oxides can alter its composition in the direction of one or two of the others without there being any major structural change, only a redistribution of ions among the tetrahedral and octahedral interstices. This accounts for their ready interconvertibility, their tendency to be nonstoichiometric, and, in general, the complexity of the Fe - O system. For further discussion of the oxides of iron, see, for example, Cotton and Wilkinson, Advanced Inorganic Chemistry, Interscience Publishers, 1966, 2nd edition, pages 847 - 862.

The second oxidation then converts at least a portion of the intermediate coating to magnetite. The exact reaction mechanism for the second oxidation has not been determined. However, the non-stoichiometric nature and easy interconvertibility of these iron compounds, as recognized by the art and as discussed in Cotton and Wilkinson, makes it reasonable to believe that the resultant black coating is composed of a mixture of iron and oxygen which only loosely resembles precise, or discrete, compounds.

The composition of the second oxidation solution can vary, depending on the type, thickness and grain structure of the prepared intermediate coating. Generally, it is considered preferable to add at least one, two or even three oxidizers and an accelerator to the second oxidation solution. The primary oxidizers may be alkali metal compounds of hydroxide, nitrate, and nitrite and mixtures thereof. Specific examples of suitable primary oxidizers include sodium hydroxide, sodium nitrate and sodium nitrite in varying concentrations. In every case, however, the overall concentration of oxidizers according to this invention is significantly lower than that seen in the conventional oxidizing processes as described in the U.S. patents cited earlier. For example, U.S. Pat. No. 3,899,367 suggests the following concentrations in the oxidizing solutions:

sodium hydroxide	200 - 1000 grams per liter
sodium nitrate	12 - 60 grams per liter
sodium nitrite	30 - 150 grams per liter.

along with minor concentrations of such additives as accelerators and wetting agents.

Actual practice in the metal finishing industry indicates that only the upper end of the concentration range shown in the above example from U.S. Pat. No. 3,899,367 is effective in producing a satisfactory black magnetite coating. Solutions of lower concentrations tend to boil at lower temperatures, leading to formation of undesirable red and brown coatings with less than satisfactory results.

1   According to the present invention, the optimal concentrations used for the second
2 oxidation solution to produce satisfactory final black magnetite coatings may be as follows:

sodium hydroxide	25 - 200 grams per liter
sodium nitrate	9 - 70 grams per liter
sodium nitrite	1 - 10 grams per liter

6   Additional components which may be added to the second oxidation solution include
7 accelerators, metal chelators and surface tension reducers. Appropriate accelerators for the
8 second oxidation include organic and inorganic nitro compounds, alkali metal compounds of
9 citrate, molybdate, polyphosphate, vanadate, chlorate, tungstate, thiocyanate, dichromate,
10 stannate, sulfide and thiosulfate, and stannous chloride and stannic chloride. Suitable
11 accelerators are chosen according to such considerations as cost and solubility. Appropriate
12 metal chelators include alkali metal compounds of thiosulfate, sulfide, ethylene diamine
13 tetraacetate, thiocyanate, gluconate, citrate, and tartrate. Suitable chelators are chosen according
14 to such considerations as cost, solubility and reactivity. Appropriate surface tension reducers
15 include alkylnaphthalene sulfonate and related compounds which are stable in high pH
16 environments.

17   A suitable accelerator for the second oxidation is selected from alkali metal salts of
18 molybdate, vanadate, tungstate, thiocyanate, dichromate, stannate, thiosulfate, stannous chloride,
19 and stannic chloride, preferably at concentrations of about 0.05 - 0.5 grams per liter. A suitable
20 metal chelator for the second oxidation is selected from alkali metal salts of thiosulfate, sulfide,
21 ethylene diamine tetraacetate, thiocyanate, gluconate, citrate or tartrate, preferably at
22 concentrations of about 1.0 - 10.0 grams per liter. A suitable surface tension reducer for the
23 second oxidation is selected from alkylnaphthalene sulfonate, typically at concentrations of about
24 0.025 - 0.2 grains per liter.

25   Suitable reaction parameters for the second oxidation are as follows: pH range: about
26 12.0 - 14.0, typically about 13.0 - 14.0; operating temperature range: about 120 - 220° F,
27 typically about 160 - 200° F; contact time range: about 0.5 - 10 min., typically about 2 - 5 min.
28 Temperatures as low as about 70 - 80 ° F at reaction times of 30 min. or more have successfully
29 been used.

30   The iron/oxygen rich intermediate coating (from the first oxidation) is responsible for
31 reducing the minimum oxidizing potential necessary for satisfactory coatings. Since the
32 substrate metal has already been oxidized by the intermediate coating solution (the first
33 oxidation), it is easier for a less powerful oxidation solution to finish the oxidation to the black
34 magnetite level (the second oxidation). The second oxidation solution is unable to react with
35 metallic iron; the second oxidation solution reacts only with the pre-existing, easily accessible
36 iron and oxygen contained in the intermediate coating. Because the intermediate coating (from
37 the first oxidation) facilitates the second oxidation reaction, a much less powerful second
38 oxidation solution is required than has been typically used in conventional blackening processes.

1   In like manner, the operating temperature and contact time for the second oxidation is
2 significantly reduced from similar parameters for conventional oxidizing solutions. Again, U.S.
3 Pat. No. 3,899,367 suggests an operating temperature of 255 - 325° F and contact times of 10 -
4 25 minutes. In actual practice, the optimal operating temperature for the process of U.S. Pat. No.
5 3,899,367 has been found to be about 285 - 295° F with 10 - 25 minute contact time. According
6 to the present invention, the optimal temperature range for the second oxidation is about 190 -
7 220° F for black coatings and about 160 - 190° F for brown coatings. Optimal contact times are
8 about 2 - 10 minutes. Both of these parameters are significantly lower than for the conventional
9 oxidizing solutions employed in U.S. Pat. No. 3,899,367.

10   Among the important advantages of the process of this invention are the suprisingly low
11 temperatures at which this second oxidation may successfully operate. Reactions at temperatures
12 as low as about 70 - 80° F produce products with highly acceptable colored surface finish,
13 generally by increasing the contact time, for example, up to about 30 min. or more. The ability
14 to successfully operate at such suprisingly low temperatures offers substantial advantages in
15 providing a process which may be safely and effectively carried out by an end user. Such 'low
16 temperature - longer time' procedures produce attractive finishes for less demanding final
17 products, including such decorative and artistic products as ornamental wrought iron work, finish
18 hardware, sculptural works, craft and artisan handworks, and similar enhancements. These
19 finishes from the 'low temperature - longer time' procedures may evidence colors in the black to
20 dark black-brown range. Further embellishment of the colored product may involve removal of
21 some of the colored finish to reveal the bright underlying metal, achieving a patina or antique
22 effect. Although it is of course known in reaction kinetics that lowering an operating
23 temperature may call for increasing reaction times, the ability to operate at such surprisingly low
24 temperatures has nowhere been reported in this industry, to the knowledge of the present
25 inventors.

26   Along with the primary oxidizing agents mentioned, the second oxidation solution may
27 preferably contain an accelerator. In the present invention, the accelerators for the second
28 oxidation solution may be alkali metal compounds of molybdate, vanadate, tungstate,
29 thiocyanate, dichromate, stannate or thiosulfate, or stannous or stannic chloride, or mixtures
30 thereof. Suitable accelerators include stannous chloride, stannic chloride, sodium stannate,
31 sodium thiosulfate, sodium molybdate and ethylene thiourea, and mixtures thereof. Other
32 accelerators which have been mentioned in prior related literature, including sodium dichromate,
33 sodium tungstate, sodium vanadate, sodium thiocyanate and benzothiazyl disulfide, all show
34 varying degrees of effectiveness in the second oxidation of this invention. In addition, surface
35 tension reducing agents tend to improve rinsability and reduce dragout from the solution.
36 Effective surface tension reducing agents include alkyl naphthalene sodium sulfonate, such as
37 manufactured by the Witco Corporation under the trademark Petro AA, and similar surface
38 tension reducing agents.

1   It is important to note that, in the second oxidation of this invention, the overall
2   concentrations of the primary oxidizers and the relative concentrations of each oxidizer in the
3   second oxidation solution are factors critical to success. It has been stated that the second
4   oxidation solution of this invention is not able to react with metallic iron, because the oxidizing
5   potential of the solution is too low. Similarly, treating a ferrous substrate, as defined above, with
6   a conventional oxidizing solution and merely reducing the concentration, temperature and
7   contact time will not result in satisfactory finishes. In general, the finishes obtained by treating a
8   ferrous substrate with a conventional oxidizing solution at reduced concentration, temperature
9   and contact time is a loosely adherent coating with an undesirable brown color. For example, the
10   oxidizing solution described in U.S. Pat. No. 2,960,420, when operated at reduced
11   concentrations, contact times and temperatures (at about 190 - 200° F) reacts poorly with the
12   intermediate coating, producing finishes which are brown and very loosely adherent. In like
13   manner, the oxidizing solutions described in U.S. Pat. No. 3,899,367 under similar operating
14   conditions also produce undesirable thin, loosely adherent brownish coatings.

15   The primary benefits derived from the process according to the present invention are not
16   related to the quality of the black finish itself, but rather to processing advantages. These
17   improved advantages include lower operating temperatures, shorter process times, and lower
18   solution concentrations, which lead to enhanced worker safety and lower operating costs. The
19   resultant black finish itself is very comparable to that of conventional blackening processes in
20   terms of corrosion resistance, wear resistance, appearance, thickness, and applications in which
21   the finished article is used.

22   The present inventive process entails the deposition of an intermediate conversion
23   coating, which is rich in iron and oxygen and represents a first oxidation of the metallic iron of
24   the substrate. This first oxidation (forming the intermediate conversion coating) is followed by a
25   second oxidation, which forms a magnetite compound by reacting with the intermediate coating.
26   The precise chemical composition of the resultant black finish has not been identified. The
27   chemical literature, as discussed above, suggests that there are three oxides of iron, all of which
28   are likely present in the intermediate conversion coating: FeO, Fe_2O_3 and Fe_3O_4 with Fe_3O_4 being
29   a mixed salt of FeO and Fe_2O_3. Besides these iron oxides, it is likely that other salts are formed
30   on the surface, including FeS, SnS, SnO in minor quantities, due to the presence of sulfur and
31   tin-based additives in the solution.

32   The first oxidation and the intermediate conversion coating formed by this invention,
33   which may be a dicarboxylate, a phosphate, mixtures thereof, or some other iron/oxygen rich
34   material, depending on the oxidation solution used, are not *per se* novel. The first oxidation and
35   the intermediate conversion coating are in fact based on known chemistry. The novelty of the
36   present invention is the use of these coatings (and the processes forming them) in the context of a
37   blackening process. The novelty of the process, and the key to its success, lies in the second
38   oxidation solution and its reaction with the intermediate coating. The concept of an initial
39   oxidation of the metallic iron, to form an intermediate dicarboxylate, phosphate or other
40   iron/oxygen enriched coating, followed by a further oxidation of the intermediate coating is a

1   novel concept in this industry and depends on the composition and operating parameters of the
2   second oxidization solution.

3   Our research to date does not indicate that the entire dicarboxylate, phosphate or other
4   iron/oxygen-enriched intermediate coating from the first oxidation is converted to iron magnetite,
5   Fe_3O_4, in the second oxidation. Rather, our experimental work suggests that the second oxidation
6   solution is reacting with molecular iron and oxygen of the intermediate coating. Although the
7   entire intermediate coating is rich in molecular iron and oxygen, it is reasonable to assume that
8   the area in which these materials are most accessible is at the top surfaces of the intermediate
9   coating crystal structure. Indeed, our tests have indicated that the black finish formed by the
10   entire process (the first and the second oxidations) of this invention can be stripped off a steel
11   article with hydrochloric acid, leaving a gray-looking finish behind. This gray-looking finish is
12   the intermediate coating. The article can then be immediately re-blackened by immersion in the
13   second oxidation solution. We have determined experimentally that the second oxidation
14   solution has no effect on metallic iron. The stripping and re-blackening experiment reasonably
15   suggests that only the top surface of the intermediate coating is turning black. If the entire
16   intermediate coating were being converted to black iron magnetite, the hydrochloric acid
17   stripping operation would remove all of the coating, down to the metallic iron, and it would be
18   impossible to re-blacken the article without first re-coating it with the intermediate coating.

19   The invention will now be further illustrated by the description of certain specific
20   examples of its practice which are intended to be illustrative only and not limiting in any sense.

21   Example 1

22   First Oxidation: A 1018 steel article is cleaned by conventional means. The cleaned
23   article is then immersed for 1 minute at room temperature in an aqueous solution containing:

24   Oxalic Acid   14 g/l
25   Phosphoric Acid   1.2 g/l
26   Sodium m-Nitrobenzene Sulfonate   6 g/l
27   Sodium Potassium Tartrate   0.4 g/l

28   The above immersion produces an opaque gray intermediate coating on the steel surface.

29   Second Oxidation: After rinsing, the intermediate coated article is immersed for 4 - 5
30   minutes at 200° F in an aqueous solution containing:

31   Sodium Hydroxide   100 g/l
32   Sodium Nitrate   35 g/l
33   Sodium Nitrite   5 g/l
34   Sodium Thiosulfate   5 g/l
35   Sodium Molybdate   5 g/l
36   Stannous Chloride   0.2 g/l
37   Petro AA   0.1 g/l

1   During this second immersion, the article gradually takes on a black color due to the
2   formation of magnetite on the surface. The article is then rinsed in water and sealed in a water-
3   displacing oil topcoat which serves as a rust preventative. The resultant coating is opaque black
4   in color, tightly adherent, with corrosion resistance equal to that provided by the topcoat oil
5   sealant.

6   Example 2

7   First Oxidation: A 4140 heat-treated steel cutting tool is cleaned and descaled by
8   conventional means. The tool is then immersed for 90 seconds at 120° F in an aqueous solution
9   containing:

10   Oxalic Acid   14 g/l
11   Phosphoric Acid   1.2 g/l
12   Sodium m-Nitrobenzene Sulfonate   6 g/l

13   The above immersion produces an opaque gray coating on the steel surface. Because the
14   4140 steel is less reactive than the 1018 steel used in Example 1, the above oxidation solution
15   has been modified from the first oxidation solution of Example 1 to eliminate the grain refiner
16   (Sodium Potassium Tartrate), and to raise the operating temperature to make the reaction more
17   aggressive.

18   Second Oxidation: After rinsing in water, the tool is immersed for 8 minutes at 200° F in
19   an aqueous solution containing:

20   Sodium Hydroxide   100 g/l
21   Sodium Nitrate   35 g/l
22   Sodium Nitrite   5 g/l
23   Sodium Thiosulfate   5 g/l
24   Sodium Molybdate   5 g/l
25   Stannic Chloride   0.2 g/l
26   Petro AA   0.1 g/l

27   During the second immersion, the tool gradually takes on an opaque black color. The
28   tool is then rinsed in water and sealed with a water-displacing rust preventative oil.

12

1 Example 3

2 First Oxidation: A mild steel decorative article is cleaned by conventional means and
3 immersed for 1 minute at room temperature in an aqueous solution containing:

Oxalic Acid	14 g/l
Phosphoric Acid	1.2 g/l
Sodium m-Nitrobenzene Sulfonate	6 g/l
Sodium Potassium Tartrate	0.4 g/l

8 The above immersion will produce an opaque gray intermediate coating on the article
9 surface after rinsing.

10 Second Oxidation: The article is then immersed for 6 minutes at 180° F in an aqueous
11 solution containing:

Sodium Hydroxide	100 g/l
Sodium Nitrate	27 g/l
Ethylene Thiourea	0.6 g/l
Tin (IV) Chloride	2 g/l
Sodium Dichromate	0.3 g/l
Petro AA	0.1 g/l

18 During the second immersion above, the article gradually takes on an opaque brown
19 color. The article is then rinsed in clear water and sealed in a clear acrylic polymer-based
20 topcoat. The resultant coating may serve as an aesthetic finish for decorative hardware, etc.

21 Example 4

22 First Oxidation: A sintered iron metal article is cleaned by conventional means and
23 immersed for 3 minutes at 120° F in an aqueous solution containing:

Phosphoric Acid	28 g/l
Hydrofluosilicic Acid	8 g/l
Xylene Sulfonic Acid	3 g/l
Dodecylbenzene Sulfonic Acid	2 g/l
Monoethanolamine	17 g/l
Sodium m-Nitrobenzene Sulfonate	1 g/l
Molybdenum Trioxide	0.2 g/l

31 After this immersion, the article has an intermediate coating of an opaque gray iron
32 phosphate deposit.

1   <u>Second Oxidation:</u> After rinsing in water, the article is immersed for 5 minutes at 200°
2 F in an aqueous solution containing:

3 Sodium Hydroxide	100 g/l
4 Sodium Nitrate	35 g/l
5 Sodium Nitrite	5 g/l
6 Sodium Thiosulfate	5 g/l
7 Sodium Tungstate	5 g/l
8 Sodium Stannate	0.2 g/l
9 Petro AA	0.1 g/l

10   During the above immersion, the article gradually takes on a black color. After rinsing in
11 water, the article is sealed in a water-displacing rust preventative oil. The resultant finish is
12 somewhat more fragile than that deposited in Examples 1 and 2, but may be considered
13 preferable for certain applications because of the expected lower operating cost. In addition, the
14 extremely porous substrate produced by this process may tend to make the fragile nature
15 unimportant, depending on the end use of the article.

16   Because of the potentially dangerous nature of the prior known metal blackening
17 processes, many manufacturers have found it more convenient to send parts to an outside vendor
18 for application of a black finish. This, of course, is inefficient and adds to the overall cost of
19 production. A particular feature of this invention is a seven-step process which may be provided
20 in a set-up of seven baths or containers, so that a metal manufacturer may safely and
21 conveniently carry out in-house metal blackening without the risk to employees posed by such
22 previous blackening procedures. The inventive process may be commercially carried out as a
23 seven step process as follows:

24   **Step 1:** The article is cleaned, degreased and descaled (if necessary) to remove foreign
25 materials such as fabricating oils, coolants, extraneous lubricants, rust, millscale, heat treat scale,
26 etc. The aim here is to generate a metal surface which is free of oils and oxides, exposing a
27 uniform and reactive metal surface. Any method of providing such a surface known to the metal
28 finishing industry is suitable. Acceptable methods include conventional cleaning in an alkaline
29 detergent soak cleaner, solvent degreasing or electrocleaning. Descaling can be accomplished by
30 acid or caustic descaling methods. Abrasive cleaning methods such as bead blasting, shot
31 peening and vapor honing may be used with good results. All these methods are well known to
32 the metal finishing industry.

33   **Step 2:** The article is rinsed in clean water to remove any cleaning residues from the
34 surface.

1   **Step 3 (First Oxidation):** The article is then subjected to a first oxidation to provide an
2 intermediate coating on the metallic iron substrate. The oxidation reagent is an aqueous solution
3 of either a dicarboxylate or a phosphate or mixtures thereof, optionally with a grain refiner, to
4 provide a water insoluble dicarboxylate-based deposit or a water insoluble phosphate-based
5 deposit, or mixtures thereof. Appropriate dicarboxylic acids include aliphatic dicarboyxlic acids,
6 generally of up to about five carbon atoms, such as oxalic, malonic, succinic, glutaric, adipic,
7 pimelic, maleic, malic, tartaric, or citric acid, and mixtures thereof. When the intermediate
8 coating is a ferrous oxalate, suitable reaction parameters are as follows: pH range: about 0.5 -
9 2.5, typically about 1.6; operating temperature range: about 50 - 150° F, typically about 75° F;
10 contact time range: about 0.5 - 5.0 min., typically about 2 min.
11

12   Appropriate reagents for deposition of the water insoluble phosphate-based coating
13 include phosphoric acid, as well as alkali metal acid phosphates, alkali metal pyrophosphates or
14 primary alkanol amine phosphates. When the intermediate coating is a iron phosphate, suitable
15 reaction parameters are as follows: pH range: about 3.0 - 5.5, typically about 4.0-5.0; operating
16 temperature range: about 60 - 180° F, typically about 120 - 130° F; contact time range: about 1 -
17 10 min., typically about 3 - 5 min.
18

19   Appropriate grain refiners include alkali metal compounds of tartrate, tripolyphosphate,
20 molybdate, citrate, polyphosphate and thiocyanate, such as sodium potassium tartrate. A suitable
21 grain refiner is sodium potassium tartrate.

22   A suitable first oxidation solution according to this invention is prepared as follows:

Component	Concentration	Acceptable Range
Oxalic acid	14 g/l	3 - 35g/l
Phosphoric acid	1.2 g/l	0.5 - 3.0g/l
Sodium m-Nitrobenzene sulfonate	6 g/l	1 - 15 g/l
Sodium Potassium Tartrate	0.4 g/l	0.1 - 2.0 g/l

23

24   Contact time in this solution is usually about 1 - 3 minutes at about 50 - 150° F. The
25 resulting deposition is an opaque, gray dicarboxylate intermediate coating.
26

15

1   Alternatively, an iron phosphating solution can be used to deposit an intermediate coating
2 which is also effective. A suitable composition and acceptable range of concentrations for this
3 option are shown below:

Component	Concentration	Acceptable Range
Phosphoric acid	28 g/l	7 - 70 g/l
Hydrofluosilicic acid	8 g/l	2 - 20 g/l
Xylene Sulfonic acid	3 g/l	1 - 7.5 g/l
Dodecylbenzene sulfonic acid	2 g/l	1 - 5.0 g/l
Monoethanolamine	17 g/l	4 - 43.0 g/l
Sodium m-Nitrobenzene sulfonate	1 g/l	0.25 - 2.5 g/l
Molybdenum trioxide	0.2 g/l	0.05 - 0.5 g/l

4

5   Contact time in this solution is usually about 1 - 3 minutes at about 80 - 150° F, resulting
6 in the deposition of an opaque, gray iron phosphate intermediate coating.

7   **Step 4:** The article is rinsed in clean water to remove any acid solution residues from the
8 surface.

9   **Step 5 (Second Oxidation):** The article is then oxidized to a colored surface by a second
10 oxidation with an aqueous solution of oxidizing agents for a time sufficient to achieve the desired
11 surface color. The composition of this second oxidation solution may include primary oxidizers
12 along with such additional components as accelerators, metal chelators and surface tension
13 reducers. Appropriate oxidizers include alkali metal compounds of hydroxide, nitrate, and
14 nitrite. The oxidizing solution for the blackening reaction (the second oxidation) preferably
15 contains three oxidizers, sodium hydroxide, sodium nitrate and sodium nitrite. If one of these
16 oxidizers is omitted, the blackening reaction has been found to proceed less efficiently.

17   Appropriate accelerators for the second oxidation include organic and inorganic nitro
18 compounds, alkali metal compounds of citrate, molybdate, polyphosphate, vanadate, chlorate,
19 tungstate, thiocyanate, dichromate, stannate, sulfide and thiosulfate, and stannous chloride and
20 stannic chloride. Suitable accelerators are chosen according to such considerations as cost and
21 solubility. Appropriate metal chelators include alkali metal compounds of thiosulfate, sulfide,
22 ethylene diamine tetraacetate, thiocyanate, gluconate, citrate, and tartrate. Suitable chelators are
23 chosen according to such considerations as cost, solubility and reactivity. Appropriate surface
24 tension reducers include alkylnaphthalene sulfonate and related compounds which are stable in
25 high pH environments.

26   Suitable reaction parameters for the second oxidation are as follows: pH range: about
27 12.0 - 14.0, typically about 13.0 - 14.0; operating temperature range: about 120 - 220° F,
28 typically about 160 - 200° F; contact time range: about 0.5 - 10 min., typically about 2 - 5 min.

16

1   A typical composition and range of concentrations for the process solution for Step 5 are
2 shown below:

Component	Concentration	Acceptable Range
Sodium hydroxide	100 g/l	25 - 200 g/l
Sodium nitrate	35 g/l	8.75 - 70 g/l
Sodium nitrite	5 g/l	1 - 10 g/l
Sodium thiosulfate	5 g/l	1 - 10 g/l
Sodium molybdate	5 g/l	1 - 10 g/l
Tin (IV) Chloride	0.2 g/l	.05 - 0.4 g/l
Petro AA	0.1 g/l	.025 - 0.2 g/l

3

4   Normal contact time for the second oxidation is about 2 - 10 minutes at about 160 - ·
5 220°F. The resulting coating may be black or brown in color, depending on exposure time,
6 temperature and composition of the oxidizing solution.

7   **Step 6:** The article is rinsed in clean water to remove any oxidizing solution residues
8 from the surface.

9   **Step 7:** The article is then sealed with a topcoat appropriate to the end use of the product,
10 such as a lubricant, a rust preventative compound or a polymer-based topcoat.

11   Cleaning and rinsing techniques, such as those described above for Steps 1, 2, 4 and 6,
12 may vary widely and are well-known to the metal finishing industry. Many different such
13 techniques can be used, depending on the condition of the metal surface prior to blackening, the
14 volume of work to be done, the finish requirements for the final finish, etc. Consequently,
15 alternate cleaning and rinsing techniques, as recognized within the metal finishing industry may
16 be used and can be determined by the operator of the process. The specific cleaning and rinsing
17 techniques described above should be considered merely illustrative.

18   Following is a description of parameters of a seven-step sequence as described above
19 used to produce a black finish on a substrate of 1018 low carbon steel panel, which exemplifies
20 operation of the process of this invention at the extraordinarily low temperature of 80° F:

21   **Step 1:** The panel is cleaned.

22   **Step 2:** The panel is rinsed.
23
24   **Step 3 (First Oxidation):** A dicarboxylate coating is provided.

25   **Step 4:** The panel is rinsed.

1   **Step 5 (Second Oxidation):** The panel is oxidized to a produce a black finish.

2   Suitable reaction parameters for the second oxidation are as follows: pH range: about
3 12.0 - 14.0, typically about 13.0 - 14.0; operating temperature range: about 80° F; contact time
4 range: about 30 min.

5   The composition and concentrations for this process solution are shown below:

Component	Concentration
Sodium hydroxide	175 g/l
Sodium nitrate	60 g/l
Sodium nitrite	10 g/l
Sodium thiosulfate	10 g/l
Sodium molybdate	8 g/l
Tin (IV) Chloride	0.5 g/l
Petro AA	0.2 g/l

6

7   **Step 6:** The panel is rinsed.

8   **Step 7:** The panel is then sealed with a topcoat appropriate to its end use, such as a
9 lubricant, a rust preventative compound or a polymer-based topcoat.